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Methods Proposed to Achieve Air Quality Standards for Mobile Sources and Technology Surveillance

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The methods proposed to meet the 1975 Standards of the Clean Air Act for mobile sources are alternative antiknocks, exhaust emission control devices, and alternative engine designs. Technology surveillance analysis applied to this situation is an attempt to anticipate potential public and environmental health problems from these methods, before they happen. Components of this analysis are exhaust emission characterization, environmental transport and transformation, levels of public and environmental exposure, and the influence of economics on the selection of alternative methods. The purpose of this presentation is to show trends as a result of the interaction of these different components. In no manner can these trends be interpreted explicitly as to what will really happen. Such an analysis is necessary so that public and environmental health officials have the opportunity to act on potential problems before they become manifest.

Technology surveillance is an attempt to anticipate potential environmental problems that may result from man's activity and his technology. Technology surveillance is my term for technology forecasting for environmental health. The main utility of technology forecasting applied to this area, is that it puts in to perspective the different proposed technical options and allows the public health official time to assess the impact of this technology on environmental health. This activity, therefore, is both probabilistic and subjective at this stage of its development.

This surveillance program is my function at the NIEHS. Because of its subjective nature, this is not an activity to be undertaken lightly, and requires the highest level of responsible scientific inquiry. If this quality of responsible inquiry is lacking, the entire activity could easily degenerate into a witch-hunt with a rapid loss of credibility and acceptance. The purposes of this conference are similar in nature: responsible inquiries about the methods which have been proposed to meet the mobile source emission standards of the Clean Air Act; and, active participation in this inquiry process, by the industries affected.

The standards of the Clean Air Act have set limits for exhaust emissions of CO, HC, and nitrogen oxides. Presently, there are no exhaust emission standards which cover emissions resulting from use of existing or new fuel additives, emission control devices, or different engine designs. We are here to discuss not only the characterization of these

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emissions and their impact on environmental health, but also strategies to minimize or eliminate adverse environmental effects.

This surveillance program on proposed methods to meet these standards began with these two questions: What would replace tetraethyllead (TEL) if this gasoline additive was banned from use? What would be the environmental effects of the exhaust emission products of this different additive? It becomes readily apparent that this is not a simple question, since there are several replacements for TEL which can achieve the same antiknock, octane-boosting function. At this point, it is appropriate to define several terms which are necessary for the discussion. Knock is defined as preignition of the fuel–air mixture during the compression and ignition strokes of the internal combustion engine. An antiknock compound competes for available oxygen in this fuel–air mixture during compression, and thus inhibits those reactions which cause preignition or knocking. Octane number is the volume percentage of isooctane (2,2,4-trimethylpentane) in a mixture with normal heptane, which as a sample fuel will give the same knocking characteristics as the gasoline in question.

Review of the available literature reveals that the removal of TEL from gasoline is not only a health consideration, but also a technical consideration with regard to the operational requirements of the catalytic muffler, which has been proposed as the major device to meet the exhaust emission standards of the Clean Air Act. In short, these initial questions rapidly expand into a consideration of the complex relationship between automotive technology, oil refinery strategy, gasoline additive science, economics, environmental transport phenomena, and human and ecological health. Figure 1 is a simplified flowchart which shows the interconnected nature of this situation, the processes involved, and the pathways to man and the environment.

On the basis of this flowchart, alternate antiknock compounds, emission control devices, alternate engine designs, their exhaust products, some aspects of the economics of changes of this type, and the effects on the environment and on human health from these alternatives will be briefly discussed. This discussion is a synthesis of literature information on all these subjects, and is an attempt to put it together with some degree of continuity, and to show the present state of knowledge on this entire subject. In this manner, it is hoped that at least a better conceptual understanding of these interconnected events can be obtained, and a realization that the actions in one area have a significant effect on the actions in another area. This type of analysis also shows that information is still needed in order to make a better assessment of the environmental impact of these alternatives. The broken line between box 1 and box 5 (Fig. 1) illustrates the partial closed-loop nature of our technological activities and their ultimate environmental impact. The outline of this presentation, therefore, is to consider each method separately, and analyze it with this loop. The main intent of this flowchart and this presentation is to illustrate the pathways to man and the environment, and will not deal with effects of exposure.

One alternative to TEL, which is presently in use, and about which there is the most information, is the use of increased percentages of aromatics. The prime aromatics used for this function are benzene, toluene, and the xylenes. Aromatics in leaded premium gasoline currently amount to about 28 vol-% and in leaded regular gasoline to about 21 vol-%. Nonleaded gasoline can contain 46 vol-% of aromatics. Therefore assuming that the total replacement of TEL by aromatics is the option of choice, the magnitude of the increase could be in the range of 12–18 vol-%.

There are several important factors which must be considered in a changeover of this type. First, the economic factor is concerned with the product redistribution and availability of basic petrochemical feedstocks. On the basis of economic considerations, it is unlikely that a higher percentage of aromatics will be chosen as a replacement for

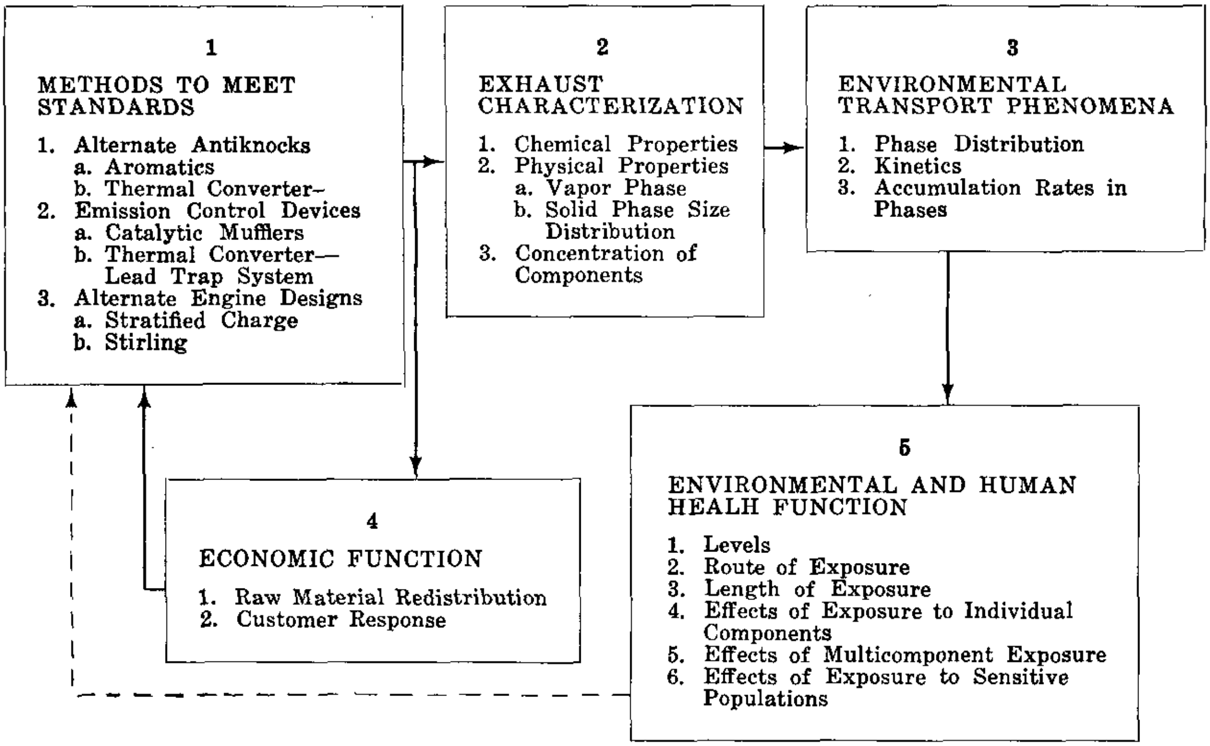

FIGURE 1. Partial closed loop used to assess the impact on the environment of alternative methods of meeting the standards of the Clean Air Act.

TEL for the following reasons: the primary source of aromatics is the refining of crude oil; these chemicals are the starting materials for many important commercial products, among them synthetic fibers and plastics; crude oil supplies are uncertain; and a small amount of TEL can accomplish the same functions as increased percentages of aromatic hydrocarbons, thus giving the refiner more options for use of refined products.

The second factor is technological. The switch to lower compression engines which do not require high octane fuels for optimum operation and the present trend towards production of the smaller engine automobiles make the option of increased aromatic use in gasoline even more remote.

The third factor is environmental. It concerns the nature of the exhaust products and their respective concentrations as a result of use of increased levels of aromatic hydrocarbons. A recent review of exhaust emissions studies (*1*) states that the main source of polycyclic organic hydrocarbons is the combustion of gasoline in the spark-ignited automobile engine. Aromatic compounds used in gasoline are precursors for polycyclic organics, and the presence of increased percentages of aromatics in gasoline increases the exhaust emission levels of these substances. From a health standpoint, the two most important polycyclic aromatics found in exhaust emissions from automobiles are the carcinogenic members of this series benzo[a]pyrene and benz[a]anthracene. It was demonstrated by the work of Gross (*2*) that raising the level of aromatics from 28%, its present level in premium gasoline with 2.5 g/gal TEL, to 46% aromatics for premium gasoline without TEL, essentially doubles the amounts of these carcinogenic compounds in the exhaust. This study also demonstrated the dramatic reduction of these two compounds in the exhaust emissions as a result of modifications in engine design and use of catalytic converters and air injected thermal converters. In effect, the change in emission levels of these compounds with emission controls amounted to a reduction of about 98% from the high-compression uncontrolled exhaust of 1966 automobiles. This reduction, however, was achieved with vehicles which had always used nonleaded gasoline. It was found that the nature of the deposit on the cylinder wall influenced the levels of polycyclic aromatics found in the exhaust. In the cases where leaded gasoline had been previously used, the reductions of polycyclic aromatics with emission controls and engine modifications were not as great. The magnitude of the reduction was approximately 30–40%. These results say something about retrofitting catalyst systems onto cars which have been using leaded gasoline, in that the reductions in polycyclic aromatics will not be as great as with cars which have always used nonleaded gasoline.

To obtain a feeling for the magnitude of concern about the release of carcinogenic materials into the environment, on assuming use of gasoline to be about 10^{11} gal–yr, and on using the data from Gross (*2*) for the use of higher percentages of aromatics (46%), the nationwide release of carcinogenic compounds could be in the range of 1000 lb/yr, if all cars were equipped with catalytic mufflers, and had always used nonleaded gasoline. This would be the nationwide lower limit. For the uncontrolled exhaust of high compression engines, on assuming all cars now fit into this classification, use of higher percentages of aromatics could release annually about 200,000 lb of benzo[a]pyrene and benz[a]anthracene into the environment. This would amount to the annual national upper level release rate of these substances. Because of their carcinogenic properties and chemical resistance to degradation in the environment, this is not a trivial concern. One of the main questions of concern to public health officials is the particle size distribution of these substances, since this determines in large part the phase that these materials are released into the environment, and ultimately the routes, rates, and levels of human exposure.

A considerable literature search indicated the most efficacious replacement additive for TEL which would provide similar octane-boosting, antiknock capabilities, was a manganese compound called methylcyclopentadienylmanganese tricarbonyl. This is not a new substance but has been produced and used since 1959. Chemically it is a penetration complex and belongs to the so-called "sandwich compounds," of which ferrocene is the best known. Optimum results were achieved with the additive when its use ranged between 0.125 and 0.25 g/gal, as compared with the use range of TEL of 0.5–2.5 g/gal, depending on the gasoline grade.

Again there are economic, technological, and environmental factors to consider in the replacement of TEL with this manganese compound. The economic factor of using additives to allow increased refinery options for raw materials is applicable for manganese. Customer response would be confined to its ability to prevent engine knock and its effect on gasoline cost.

The literature presently available says very little about the technological aspects of how this compound performs the antiknock function. But it probably oxidizes very rapidly and competes for oxygen, and thus inhibits preignition reactions in much the same manner as TEL. In the environmental assessment of manganese as a replacement for TEL, the most important questions are the chemical nature of the exhaust products and the size distribution of these particles. According to information published by Ethyl Corporation (*3*), manganese exhaust particulates have similar size characteristics as lead exhaust particulates. Chemically, these particulates have been identified as Mn_3O_4 by x-ray diffraction. In this reported study, the level of manganese added to gasoline was 0.125 g/gal.

Once discharged into the environment, the ultimate fate of the manganese becomes the important issue, i.e., the environmental transport and transformation processes which dominate. By using methods similar to those employed by Huntzicker and Friedlander (*4*) in their study of flow of automobile emitted lead through the Los Angeles Basin, it may be possible to estimate levels of manganese exhaust products in different phases. In particular, the levels and chemical structure of suspended manganese oxides are of great importance since it has been demonstrated in work reviewed by Sullivan (*5*) published in 1969, that MnO_2 catalyzed the liquid-phase oxidation of SO_2 to SO_3. SO_3 was then hydrolyzed to sulfuric acid. The rate of conversion of SO_2 to sulfuric acid by this heterogeneous process increased as the concentrations of SO_2, manganese dioxide, and water vapor increased. If it was assumed that the particle size distribution of suspended MnO_2 was very narrow, it then appeared that the adsorption of SO_2 was rate-controlling, since the rate increased as the partial pressure of SO_2 increased.

The mention of the heterogeneous conversion of SO_2 to SO_3 leads into the questions which have been raised about one of the emission control devices: the catalytic converter. This device appears to be the method to be employed on 1975 automobiles to meet regulated exhaust emission levels.

Campion (*6*) demonstrated in 1973 that the platinum metal of the catalytic muffler was a very efficient surface for converting residual sulfur in gasoline to SO_3. Therefore, if this device is used, desulfurization of gasoline, along with removal of lead, will be required to minimize SO_3 formation and ensure the catalyst life. In effect, by choosing this alternative, not only will regulated emission standards be met, but unregulated emission of SO_3 and lead to the environment will be eliminated. Such a complex series of events could mean major economic and technological changes in industry, and it would be most important to know what the coordination and timetables for these changes would be.

Other unanswered economic and technological questions about the catalytic muffler were raised by the National Academy of Sciences report (*7*) of the Committee on Motor Vehicle Emissions. In particular, questions were raised about the engineering feasibility and lifetime of the device, and the ability to maintain and service properly vehicles equipped with these devices. Because this is an add-on device, additional concerns are: the effect of these devices on engine operating temperature; the modifications in engine cooling capacity required; and, the concomitant loss involved in engine efficiency and engine life.

In my opinion, emission control devices are approaching the problem of air pollution from mobile sources, from the wrong end. There should be more of an effort to redesign the sources of the problem—the engine and the gasoline.

Environmental questions which have been raised about the proposed use of the catalytic converter concern the rate of breakup of this platinum-on-alumina catalyst and the discharge of these substances, how the loss of catalyst materials affects removal capacity of these devices, the chemical structure of emitted substances, and their ultimate environmental fate. It is also unknown what other reactions can occur on this platinum surface at the high normal exhaust temperature in a reducing followed by an oxidizing atmosphere.

Another proposed emission control device is the thermal converter–lead trap system. The volume of information written about the advantages and disadvantages of this device, in comparison with the amount written about the catalytic muffler is minuscule. Here is a device which does not require major procurement of the expensive metals, can be used with existing leaded gasoline blends, reduces regulated emissions to acceptable levels, and reduces lead emissions by 80–90%, or from an average of 0.14 g/mile to 0.018 g/mile. With this device, there is the option of reducing a known series of exhaust products to lower levels, rather than the possibility of having to deal with an entirely new series of unknown exhaust products. This should not be taken as an endorsement of this device over the catalytic muffler. However, the opportunity to reduce lead emissions by 80–90% is not an option to be dismissed lightly, and certainly requires more discussion than has been witnessed up to this point.

What may be happening in this instance is the inability of decision-makers to change their opinion. Once a choice has been made, it has its own momentum which carries it along, with the associated refusal or inability to hear contrary or dissenting opinion.

With regard to alternative engine designs, the Compound Vortex Controlled Combustion (CVCC) engine or stratified-charge engine appears to reduce the levels of regulated emissions to acceptable levels without the need of the catalytic muffler. If this engine can achieve these standards without loss of performance and fuel economy, I believe these would be very strong arguments for proceeding in this direction. Again, characterization of unregulated exhaust emissions is required to complete the analysis of whether or not this engine truly solves important environmental problems.

Another alternative engine design which has received very little discussion is the Stirling engine. It is apparently more economical to operate, since it can run on lean air–fuel mixtures, is quieter, and with exhaust recirculation can meet the regulated emission standards of the Clean Air Act. As with the CVCC engine, characterization of unregulated exhaust emissions is necessary to complete the analysis of this engine's ability to solve important environmental problems.

In summary, I have described the application of technology surveillance to a consideration of the methods proposed to meet the exhaust emission standards of the Clean Air Act. The inquiry into this question began with the determination of the most efficacious replacement of TEL and expanded into consideration of the economics involved in making a replacement of this type, characterization of exhaust emissions, environmental transport processes involved, and the level of chronic exposure to man and the environment. This surveillance program is important since it allows public health officials the opportunity to act on potential problems before they become manifest.

Because of the magnitude of this task, it must be a combined effort of both industry and public health agencies. The discussions of this effort must also be characterized by a degree of candor and objectivity unparalleled in recent experience. This critical analysis must also consider the following larger questions:

- What are our limits to technical and population growth?
- Where is the automobile industry going—indeed, will there be an automobile industry in 30 years?
- Can we afford to delay action on environmental health until we have proved the existence of an adverse effect beyond a shadow of doubt?
- What does our growth in industry and population mean in terms of raw materials, food, and human resources?

As one popular commercial says, "We're all in this together."

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